Carbon burial over the last four millennia is regulated by both climatic and land use change

Carbon burial over the last four millennia is regulated by both climatic and land-use change

Running title: Controls on millennial-scale carbon burial

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Abstract

Carbon sequestration by sediments and vegetated marine systems contributes to atmospheric carbon drawdown, but little empirical evidence is available to help separate the effects of climate change and other anthropogenic activities on carbon burial over centennial time scales. We used marine sediment organic carbon to determine the role of historic climate variability and human habitation in carbon burial over the past 5071 years. There was centennial-scale sensitivity of carbon supply and burial to climatic variability, with Little Ice Age cooling causing an abrupt ecosystem shift and an increase in marine carbon contributions compared to terrestrial carbon. Although land use changes during the late 1800s did not cause marked alteration in average carbon burial, they did lead to marked increases in the spatial variability of carbon burial. Thus, while carbon burial by vegetated systems is expected to increase with projected climate warming over the coming century, ecosystem restructuring caused by abrupt climate change may produce unexpected change in carbon burial whose variability is also modulated by land use change.

Introduction

Coastal ecosystems represent <10% of Earth biomes (Costanza & Folke, 1997) but they play a disproportionately important role in the global carbon cycle (Bauer et al., 2013). Drawdown of atmospheric CO_2 into the coastal ocean enables CO_2 sequestration into organic tissues by photosynthesis and subsequent lock-down into sediments as sediment organic carbon (SOC) (Barbier et al., 2011; Nellemann et al., 2009). This so-called blue carbon sequestration by vegetated marine systems accounts for 50% of total marine C burial (Duarte, Middelburg, & Caraco, 2005), with fjordic sediments accounting for at least 11% of global C burial (Smith, Bianchi, Allison, Savage, & Galy, 2015), and is recognised as a potential long term store by the Intergovernmental Panel on Climate Change (IPCC) (Kennedy et al., 2013). While it is expected that climate warming may increase carbon sequestration by vegetated marine systems (Marbà, Krause-Jensen, Masqué, & Duarte, 2018), little empirical evidence is available to help separate the effects of climate change and other anthropogenic activities on carbon burial over centennial time scales. Such effects include the varying influences of alteration in allochthonous carbon sources, land use and climatic change (Fourqurean et al., 2012; Krause-Jensen et al., 2018). For example, while in terrestrial systems modelling the impacts of land use changes on carbon dynamics is increasing, in marine system climate models land use change is generally excluded (Ciais et al., 2014).

Our knowledge of carbon burial by coastal systems is greatest in their quantification, largely assessing marine habitats dominated by seagrass (e.g. (Duarte et al., 2005; Kennedy et al., 2010; Marbà et al., 2018)), salt marshes (e.g. (Chmura, Anisfeld, Cahoon, & Lynch, 2003; Kirwan & Mudd, 2012)) and mangroves (e.g. (Alongi, 2012; Bouillon et al., 2008)), SOC stored in deposits created by calcifying coralline macroalge (Trevathan-Tackett et al., 2015; van der Heijden & Kamenos, 2015) and marine sediments storing allochthonous carbon (Smeaton et al., 2016; Smith et al., 2015). These studies have demonstrated the comparable carbon storage capacity of coastal systems to the more widely studied carbon storage ecosystems on land (e.g. rainforests) (Pidgeon, 2009). This is particularly pertinent given the temporal range over which many marine carbon repositories exist (centuries to millennia), and thus their long-term carbon accumulation potential. Over that period, biotic activity within the carbon repositories themselves can directly affect a system's capacity for carbon sequestration and burial (Mcleod et al., 2011). Additionally, damage to those systems has the capacity to not

only prevent sequestration but also to mobilise carbon that had been previously stored for millennia (Fourqurean et al., 2012).

Coralline algal ecosystems are a biodiverse habitat created by calcifying algae that support multiple trophic levels (Steller, Riosmena-Rodriiguez, Foster, & Roberts, 2003) and have recently been highlighted as a potentially large blue carbon repository (Burrows, Kamenos, Huges, et al., 2014; van der Heijden & Kamenos, 2015). Coralline algal ecosystems are globally distributed (van der Heijden & Kamenos, 2015) and the accreted deposits they create are stable over millennia (e.g. since the early Cretaceous (Aguirre, Riding, & Braga, 2000), enabling burial and storage to occur over geological timescales. Organic carbon stored in these ecosystems is predominantly allochthonous, trapped by the complex three-dimensional nature of the algal thalli leading to deposit accretion (van der Heijden & Kamenos, 2015). Current estimates suggest net global primary production of 173 g C m^{-2} yr^{-1} by the coralline algal component of the ecosystems (van der Heijden & Kamenos, 2015), although at present little empirical information is available on carbon burial and the balance between calcification and burial.

Here, we investigated (1) the roles of centennial scale climate and land use change in driving marine SOC accumulation and variability, (2) the longevity of carbon burial and (3) the roles of ecosystem change in driving carbon burial and variability. For this we used Loch Sween, Scotland, which has a well-defined land use history over several centuries (see Supplementary Material), is influence by major climatic variation and sequesters and stores allochthonous and autochthonous carbon in a coralline algal deposit. Sediment cores were dated using radiocarbon, and isotopic composition and C/N ratios of SOC and contemporary terrestrial / marine source end-members were determined to generate SOC stock, organic carbon source and C/N time series.

Materials and Methods

Study system

The coralline algal ecosystem is a highly biodiverse habitat that supports multiple trophic levels (Steller et al., 2003) and has been highlighted as a blue carbon repository (Burrows, Kamenos, Hughes, et al., 2014; Trevathan-Tackett et al., 2015; van der Heijden & Kamenos, 2015).

Coralline algal beds are globally distributed (van der Heijden & Kamenos, 2015) and are stable over millennia (e.g. since the early Cretaceous (Aguirre et al., 2000)), enabling burial and storage to occur over geological timescales in the sediments they trap.

Study site and core sampling

Cores (n = 3, 11 cm diameter) were collected from a live coralline algal bed in Loch Sween (Figure S1), on the west coast of Scotland at a water depth of ~6 m. Core locations were spread across the coralline algal bed (core 1 = nearest the loch head [86 cm core length], core 2 = center of the bed [71 cm core length], core 3 = nearest the loch mouth [80 cm core length]). Cores were collected using a slide hammer and SCUBA, kept in an upright position and frozen immediately on return to shore (within 20 minutes of collection).

Historic land use change

Arichonan (~100 residents) was previously situated at the head of Caol Scotnish and was the primary source of nutrients into the loch. It is thought to have begun as a settlement which farmed livestock and grew crops in the 1600s. Major changes in habitation did not happen until 1848 when the population of Arichonan became largely uninhabited over the following 5 years due to tenant evictions during the Highland Clearances (James, 2009).

Age model

Five new radiocarbon data points for Core 2 are presented in Table S1. Prior to radiocarbon dating, suitable coralline algal thalli or shell material was selected from Core 2. For each coralline algal thallus, a branch tip containing approximately 20 bands (= equivalent years of growth), was selected for analysis. Shell fragments were selected as found. Surficial calcareous encrustations were removed where necessary and the sample subjected to ultrasonic agitation in distilled water to remove detrital particles then oven dried (40 °C). In conjunction with radiocarbon dates from Core 1 (Kamenos, 2010), these new data points were used for age model construction, resulting in an age record for the past 5071 calibrated years (Tables S1 & S2).

Radiocarbon analysis was conducted at the NERC Radiocarbon Facility-East where the outer 20% by weight of sample material was removed using dilute HCl. Samples were then rinsed in distilled water, dried, ground and converted to CO_2 via hydrolysis with 85% H_3PO_4. Sample CO_2 was cryogenically purified and an aliquot converted to graphite via Fe/Zn reduction (Slota,

Jull, Linick, & Toolin, 1987). Graphite was submitted to the SUERC AMS Laboratory, where sample $^{14}C/^{13}C$ ratios were determined using a NEC 250 kV SSAMS accelerator mass spectrometer (Freeman, Dougans, McHargue, Wilcken, & Xu, 2008) and measured to 3‰ counting precision.

All results were appropriately background corrected and normalised to $\delta^{13}C_{VPDB}$‰ of -25 according to the conventions described in (Stuiver & Polach, 1977). $\delta^{13}C$ concentrations were determined using a Themo Finnigan Delta V Duel-Inlet and are representative of the $\delta^{13}C$ of the original, pre-treated sample material.

Conventional years BP (pre-1950 AD), calibrated age ranges (BC/AD) and calibrated years BP are presented in Tables S1 and S2. Associated errors (one sigma) include components from the counting statistics on the sample, modern reference standard, process blank and instrumental error. Calibration to calendar years was conducted with OxCa1 version 13 (Bronk Ramsey, 2009) using the Marine13 (Reimer et al., 2013) radiocarbon age calibration curve. Local deviations in the Marine Reservoir Effect were accounted for using a Delta-R of -47 ± 52 as suggested by (Russell, Cook, Ascough, & Scott, 2015). Core tops all had live coralline algal growth so were assigned a 0 years age (2015). Linear interpolation was used between dates and as the oldest part of the cores contained no datable material, linear extrapolation beyond the dated range was also used to estimate their age.

The ^{14}C age model was further tuned using magnetic susceptibility (MS) performed on all core horizons (Figure S2). Direct measurements of MS (Bartington MS3E, 3.8mm spatial resolution, e.g. (Peti & Augustinus, 2019; van der Bilt et al., 2018)) were made on the flat surface of core horizons at the central portion of the core. The horizon surface was tightly covered by a single layer of plastic film during the measurement to prevent sensor contamination. Six contiguous measurements were taken on each horizon and considered as averages ± SD. The sensor was calibrated after each measurement following manufacturer specifications.

End-member sampling for isotopic calibration

End member samples were collected at the sample site to enable fingerprinting of the SOC source. These included: soil (up to 15 cm depth, n = 5 along an altitude gradient from the shore),

terrestrial plants common to the area (7 species, Table S3), partially degraded leaves found within the coralline algal bed (only *Quercus petraea* leaves were found), water column particulate organic matter (POM) (0.2 µm seawater filtrate, n = 5), marine macroalgae (10 species, see Table S4) and marine invertebrates (4 species, Table S3). Terrestrial samples were frozen immediately on collection. Marine macroalgae were gently cleaned following collection, rinsed with deionized water and frozen. Marine invertebrates were depurated in filtered seawater for 12 hours following collection, before being rinsed with deionized water and frozen.

Sample preparation

Each sediment core was cut into 2cm horizons whilst still frozen. Each horizon was then dried at 60°C for three days and sieved into three size fractions for subsequent SOC analysis (<63 µm, 63-250 µm, 250-500 µm). Each fraction was ground into a fine powder using a ball mill and a small portion was acidified (5N HCl). Carbonate specimens (e.g. fragments of shell or coralline algae) were picked from the >500 µm fraction for ^{14}C dating (described above). All isotopic end member samples were oven dried at 60°C for three days and ground into a fine powder. Half of each powdered sample was then acidified to remove carbonate material (5N HCl), before rinsing with deionized water and drying for a second time.

Stable isotope analysis

$\delta^{13}C$ and $\delta^{15}N$ stable isotope analyses was conducted at the NERC Life Sciences Mass Spectrometry Facility (at SUERC) to identify the primary source(s) of organic matter in each sediment horizon. This enabled discrimination between terrestrial / marine inputs and trophic levels via comparison to the end member samples (e.g. (Graham, Eaves, Farmer, Dobson, & Fallick, 2001; Macreadie, Allen, Kelaher, Ralph, & Skilbeck, 2012; Thornton & McManus, 1994)). Since marine organisms are distinctly less cellulosic but more proteinaceous than terrestrials, C/N ratios have also been widely used for reflecting physical mixing of sediment material composited by distinct end member sources. A marine algal dominated source of sediment material is represented by C/N ratios of 4-10 (Meyers, 1994); C/N ratios >12 represent terrestrial vascular plant end member sources (Lamb, Wilson, & Leng, 2006). All analyses were carried out using a Delta Plus XP continuous flow isotope ratio mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) coupled to a Pyrocube Elemental Analyser (Elementar, Langenselbold, Germany). Three laboratory standards (Gelatine, Alanine/Gelatine and Glycine/Gelatine) were analysed for every 10 unknowns and used to

correct for instrument drift during each analytical run, which typically lasts 16 hours. Four aliquots of USGS50 were analysed each day (average and standard deviation for USGS 40 over 6 analytical runs, spanning a period of 6 months (n=24) was $\delta^{13}C$ -26.35 +/- 0.13‰ and $\delta^{15}N$ -4.60 +/- 0.20‰, accepted values are -26.39 +/- 0.04‰ and -4.52 +/- 0.06‰ respectively). While $\delta^{13}C$ analyses were possible for all sediment fraction sizes, only the <63 µm fraction had sufficient N to accurately determine $\delta^{15}N$. SOC mass was quantified via weight percentage of organic carbon (OC%) and total carbon (TC%), determined by mass spectrometry.

$\delta^{13}C$ and $\delta^{15}N$ were determined in each 2 cm horizon of core 1, providing a 20-40 year resolution. For cores 2 and 3, analytical limitations prevented analysis of all the horizons: from 860-150 calBP 20-40 year resolution was achieved, while horizons older and younger than this period were analysed at up to ~180 year resolution (Table S2).

In situ seawater temperature

A fortnightly 653-year reconstructed in-situ water temperature (IST) record for Loch Sween is available from Kamenos (2010), enabling a direct comparison between IST and carbon storage at the same location.

Calculation of C stock

Areal carbon storage (Mg Ha^{-1}) was quantified using weight % organic carbon (OC), the mass of the horizon and the core surface area:

$$SOC_{stock} = \sum_i S_i \times A$$

where, i refers to the three fractions of sediment, S_i is total SOC stock, and A is the core surface area. The SOC stock of each horizon was calculated as:

$$S_n = WT_n \times W_n$$

where, n refers to the core horizon, WT is the weight percent of OC in each horizon, and W is the total mass of each horizon.

Statistics and isotopic mixing model

Data analysis was conducted in R (version 3.3.2: One-way ANOVA and Pearson correlation coefficient). The segmented package (Muggeo, 2008) was used for breakpoint regression

analysis, the Stable Isotope Analysis in R (SIAR) mixing model package (Parnell, 2013) for stable isotope mixing models and ggplot2 (Wickham, 2010) for visualizing data. Cross-wavelet coherence analysis was used to describe time series and compare marine in situ temperature with carbon metrics; analyses were conducted in R using the WaveletComp package (Roesch & Schmidbauer, 2014).

Results

Both organic carbon (OC) and total carbon (TC) showed a decreasing trend from the present day to ~400 calBP (Figure 1), accompanied by a distinct diversion of OC and TC during the period 400-250 calBP. As would be expected, a degree of SOC remineralisation was observed (indicated by a general decline in OC over time): this was apparent for the last ~400 years, prior to which the quantity of buried organic carbon stabilized to a constant, but lower, concentration.

While there is little evidence of a change in mean TC and OC directly after 1848 (~125 calBP), when the local habitation and livestock husbandry at Arichonan ended abruptly, there is a notable increase in OC standard deviation during the period ~1848-1950 calAD (~125-0 calBP). Both TC and OC both show a marked narrowing of SD in ~125calBP (1848-50 calAD) and also ~420 calBP (~1625 calAD) (Figure 1). While these relatively short periods of reduced SD are do not directly link with troughs in IST (Figure 1), there is evidence of wider coherence between IST and OC as well as inorganic carbon (IC) and TC with a 65y period between 320-220 calBP and 150-0 calBP, and a 150y period from 250-150 calBP ($P < 0.05$).

Temporal change in the source of organic carbon

The baseline end members provide a distinction between marine / terrestrial inputs, and across trophic levels (Figure 2). The $\delta^{13}C$ / $\delta^{15}N$ composition of the sediment fell into two discrete temporal periods (Figure 2); this temporal change was consistent across all cores. Prior to ~370 calBP, the organic matter was characterised by lower $\delta^{15}N$ (<6.0‰, Figure 2) and there was evidence of higher C/N elemental ratios (increased SD) (Figure 3) typical of terrestrial C3 plants, suggesting that terrestrially-derived carbon was an important component of the total organic carbon pool in this system until ~370 calBP (macroalgal-derived organic material

(40%), terrestrial plants (28%), terrestrial soil (21%) and marine fauna (11%) (Figure S5)). $\delta^{15}N$ during this period remained relatively constant. In contrast, sediments deposited more recently than ~370 calBP were characterised by higher $\delta^{15}N$ and $\delta^{13}C$ typical of marine algae and fauna (Figure 2) and C/N elemental ratios were also indicative of marine-derived sources (Figure 3), suggesting a recent transition towards a dominance in marine-derived organic carbon (marine fauna (~42%), macroalgae (~27%), terrestrial plants (~24%) and terrestrial soil (~8%) (Figure S5)). Additionally, more recently than 370 calBP $\delta^{15}N$ was characterised by a significant increase over time ($F_{1,40}$=30.1, $p<0.001$; Figure S4), suggesting a temporal increase in the proportional contribution of higher trophic levels to the carbon stored (i.e. derived from marine consumers, e.g. marine invertebrates). $\delta^{13}C$ variation showed a general increase over time ($F_{1,71}$=105.9, $p<0.001$; Figures 2 & S3), but no clear temporal groupings in the dataset were observed. The major change in isotopic composition during ~370 calBP occurred directly after the marked drop in the in-situ temperature, but at least 200 years before the major change in habitation at Arichonan during 1848 (Figure 1). Partially degraded leaves found in the coralline algal bed were enriched in $\delta^{15}N$ compared to their terrestrial counterparts although they still remained in the 'terrestrial' envelope. Water column particulate organic matter lay between the marine-derived and terrestrially-derived inputs (Figure 2).

Bulk carbon stock

Organic carbon in coralline algal systems is associated primarily with the SOC buried in the open matrix carbonate deposits that are created by the calcifying organisms (van der Heijden & Kamenos, 2015). Within the upper 25 cm of sediment, 7.23±1.30 (mean±SD) Mg OC Ha^{-1} were stored in the coralline algal bed (Figure 4). This is similar to temperate Australian seagrasses (Lavery, Mateo, Serrano, & Rozaimi, 2013) but is higher than estimates for high latitude kelp forest standing stock (1.41±0.66 Mg C Ha^{-1}) (Burrows, Kamenos, Hughes, et al., 2014) and the average for high latitude marine sediments (2.51±2.1 Mg C Ha^{-1}) (Burrows, Kamenos, Hughes, et al., 2014). Across the full depth of the cores, the total organic carbon (TOC) stock of the coralline algal bed was 12.28±1.98 Mg OC Ha^{-1}. Thus, ~60% of the TOC stock was stored in the top 25 cm of the deposit.

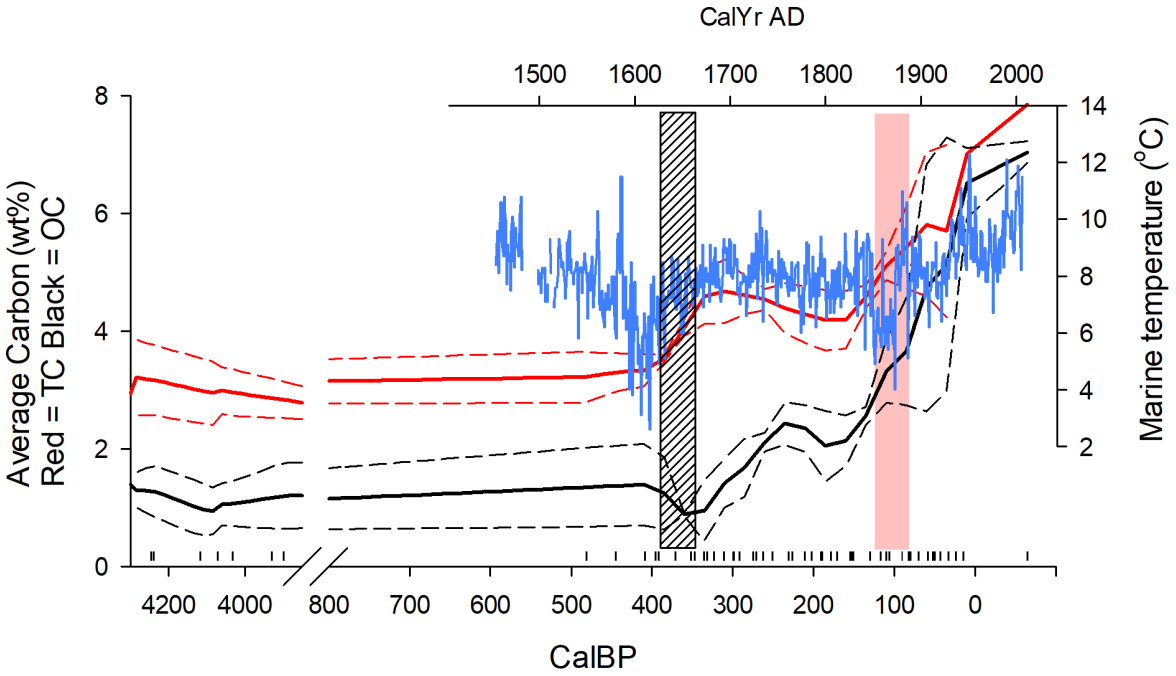

Figure 1 Average total carbon (TC, red line, n = 3 per time point), organic carbon (OC, black line, n = 3 per time point) and marine temperature (blue line). Dashed lines represent SD. Vertical rug on x axis defines calBP age of each core section used in TC and OC determination. Blue line represents in situ reconstructed marine temperature of the sampling site (Kamenos, 2010). Black diagonal shading indicates period of proposed ecosystem reorganization (from Fig 2). Red shading indicates timescale of abrupt land use change.

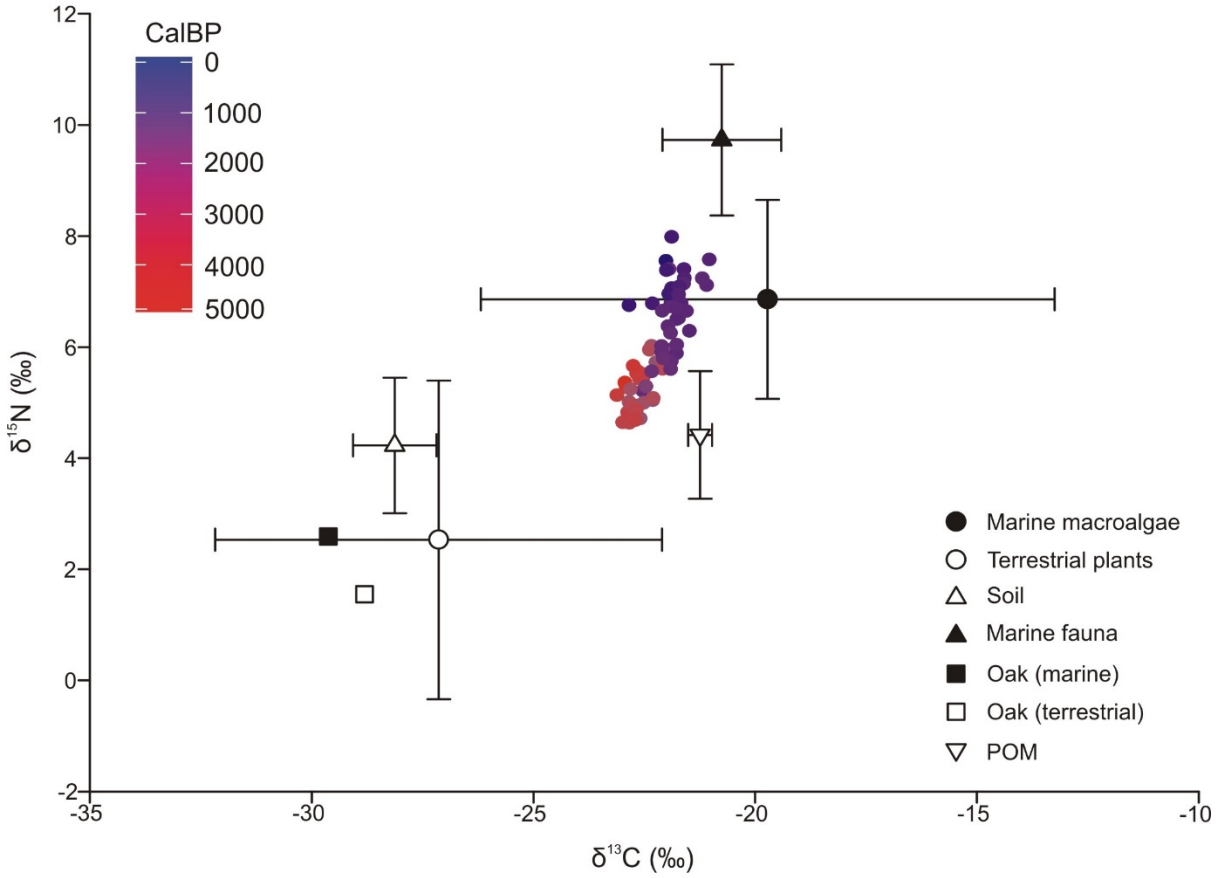

Figure 2 $\delta^{13}C$ against $\delta^{15}N$ (‰) of core organic material (<63 µm size fraction, coloured points, colour-coding = sediment age) and end-members (black/white symbols, mean±SD). 'Oak (marine)' refers to fallen oak leaves that were collected underwater from within the coralline algal bed framework. Oak was represented by 1 terrestrial and 1 marine sample so no SD presented. POM = particulate organic matter.

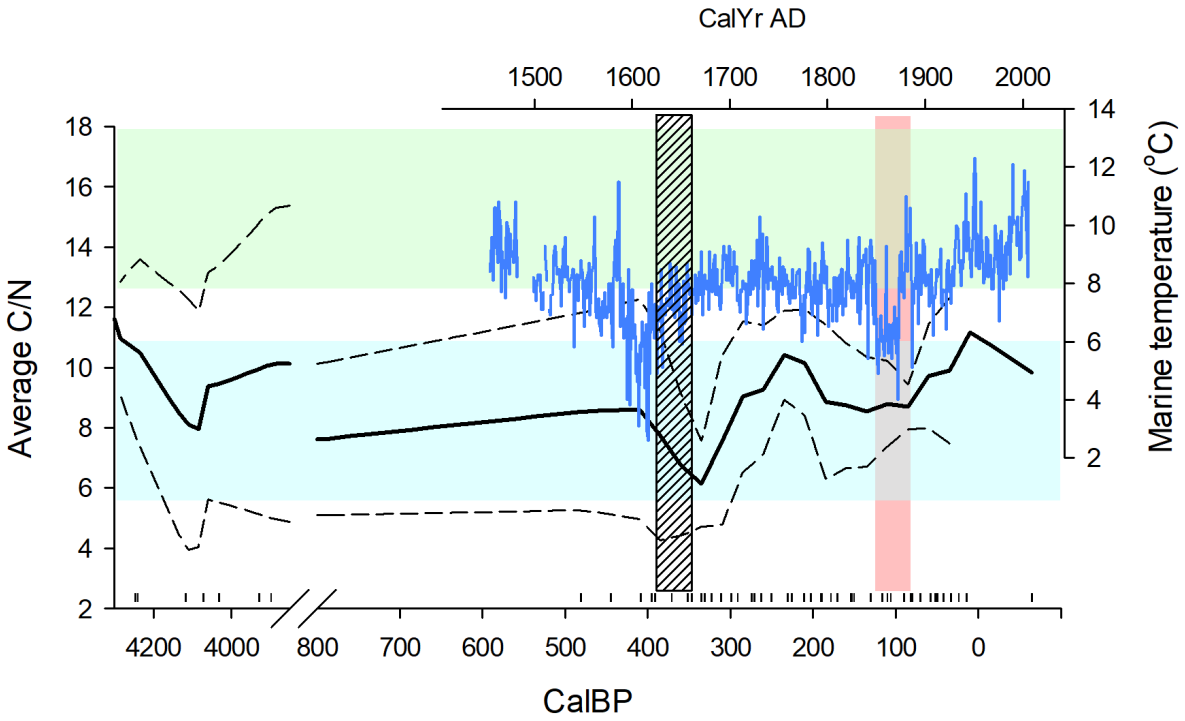

Figure 3 Soil organic material C/N elemental ratio (mean (n = 3 cores; solid line) ± SD (dashed lines)) and marine temperature (blue line; from Kamenos (2010)) over time. Vertical rug on x axis defines calBP age of each core section used to calculate C/N. Blue horizontal shading represents typical marine algal C/N ratios as defined in (Meyers, 1994). The green horizontal shading represents typical terrestrial plant C/N ratios, as defined in Lamb et al (2006). Black diagonal shading indicates period of ecosystem reorganization (from Fig 2). Red shading indicates timescale of abrupt land use change.

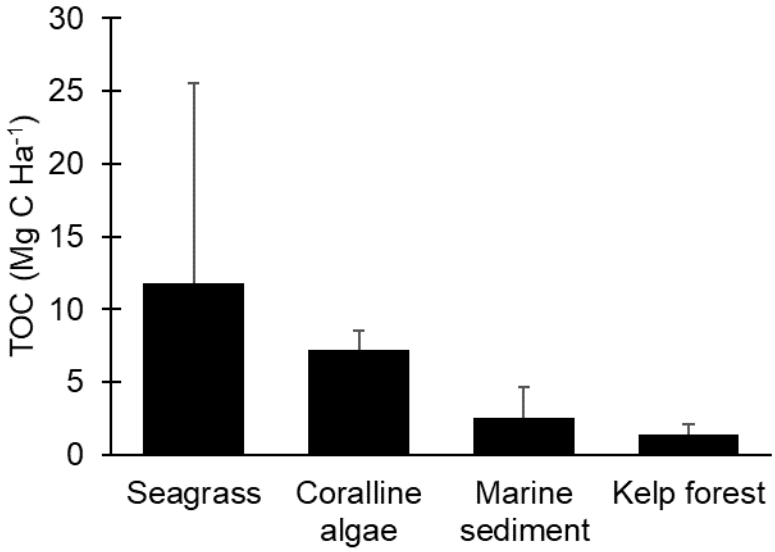

Figure 4 Sediment organic carbon stock (TOC Mg C Ha^{-1}) in systems classified as blue carbon repositories. Average concentrations (+SD) for top 25 cm of seagrass mats, including above-ground biomass (Lavery et al., 2013), the top 25cm of coralline algal deposits (this study) and top 25 cm of marine sediment (Burrows, Kamenos, Hughes, et al., 2014), and above-ground kelp biomass standing stock (Burrows, Kamenos, Hughes, et al., 2014).

Discussion

Here we show evidence of the influence of both historic temperature and land use changes on carbon accumulation at centennial time scales. The distinct period of low OC accumulation (starting ~370 calBP) directly followed the onset of environmental cooling during the mid-LIA temperature minimum (e.g. (Asteman, Nordberg, & Filipsson, 2013; Cage & Austin, 2010; Kamenos, 2010)), while wide variability in OC burial follows major land use changes after 125 calBP.

Climate and land-use regulation of carbon burial

The coherence between OC and historic temperature variability may be driven by a decrease in organic production during periods of reduced temperature because of (1) a decrease in the metabolic rates of marine organisms (Nwewll & Northcroft, 1967) and / or (2) reduced terrestrial runoff during cooler phases, reduced nutrient delivery to marine systems and a

subsequent reduction in primary productivity (Szczuciński, Zajączkowski, & Scholten, 2009). This is supported by the abrupt change in the source of organic matter around ~370 calBP (Figure 2), characterised by a rapid increase in the proportional dominance of marine-derived matter and a reduction in terrestrially-derived matter. It is possible that the biological pathways linking carbon burial and climate coherence at 65y and 150y periods differ; those driving 65y period coherence being sensitive to temperature reduction while those at 150y period breaking down at higher temperatures seen during the last century (Figure 1).

Our data suggests a large, climate-driven, ecosystem shift that occurred at ~370 calBP, supported by three lines of evidence: (1) an abrupt increase in the proportion of carbon from higher trophic levels in younger sediments (Figures 2 & 3), (2) an increase in the contribution of marine-derived matter to the carbon stock in younger sediment, compared to a higher dominance of terrestrially-derived matter in older sediment (Figures S5) and (3) absence of a dramatic change in sediment composition (Figure S2), indicating that (1) and (2) happened locally and were not due to a new source of organic material derived at distance from the site. Disturbance and reorganization of ecosystems due to temperature changes are known in marine ecosystems (Gutierrez et al., 2009) and, more widely, in terrestrial ecosystems (Nolan et al., 2018); these changes can involve replacement of dominant organisms / functional types and be accelerated by other interacting processes (Hughes et al., 2007; Overpeck, Rind, & Goldberg, 1990). Our data suggest that the ~370 calBP LIA-triggered ecosystem shift was associated with a relative decrease in marine productivity followed by an increase in productivity (excluding the longer-term trend driven by background remineralisation, Figure 1), further supported by the C/N ratios which become more marine after the temperature minima during the LIA (Figure 3). This may be associated with a shift to a larger proportion of calcifying biota (other than the coralline algae themselves), evidenced by the divergence in TC and OC beginning around 400 calBP. Notably, there is a ~50 year lag between the change in climate and the peak of ecosystem restructuring; such lags in response to climate change have also been recorded in other terrestrial and marine ecosystems and can be related to variable sensitivities of different parts of the ecosystem and associated interacting factors including population size, dependence on prey availability and resource competition (Camill & Clark, 2000; Poloczanska et al., 2016). In Caol Scotnish, this lag may be further enhanced by such interacting ecosystem processes occurring in both terrestrial and marine sources of organic material.

Just after the 125 calBP (1848-50 calAD) cooling period, OC standard deviation abruptly increased, reaching the largest SD in the record, until 0 calBP (~1950 calAD) before gradually reducing to 2015. We interpret this widening of responses as divergent influences of climate and land use changes due to human habitation on carbon burial. In 1848 the village of Arichonan (the primary source of anthropogenic inputs to Caol Scotnish) was abandoned abruptly during the Scottish Highland clearances, leaving the farmed land to rewild from its previous use in animal husbandry and arable agriculture. Our data suggest land use changes led to markedly variable organic carbon inputs, possibly due to changes in runoff patterns and the source of allochthonous carbon. This caused increased heterogeneity in carbon burial while not necessarily changing the mean quantity of carbon buried. Further, a component of that increased variability may be caused by subtly different rates of temporal organic carbon breakdown and remineralisation across the coralline algal bed during that period. Although there are two distinct periods of very reduced SD in TC and OC, these are not consistently associated with distinct climatic patterns so, given the number of replicate cores (n=3), we attribute them to chance.

In this system, land use change to farming was gradual, followed by abrupt rewilding. However, there is evidence that where habitats are damaged, losses of carbon from vegetated wetlands can be linked to eutrophication (e.g. wetlands (Hopkinson, Cai, & Hu, 2012)), dredging (seagrass (Greiner, McGlathery, Gunnell, & McKee, 2013)) as well as natural disturbances for exposed repositories including hurricanes (e.g. mangroves (Barr, Engel, Smith, & Fuentes, 2012)). Although we have little empirical evidence available for specific changes in land use during the period over which Arichonan was inhabited, the notable drop in carbon burial during 180 calBP – at which time there is no obvious thermal driver – may be due to negative changes in land use practices. Such variability in carbon release caused by changes in land use, and the way this is modelled, is a driver of differences between climate models, but this currently is not well integrated into marine modeling approaches (Ciais et al., 2014).

Role of calcifying algal systems in carbon burial

Relatively little is known about the role of calcified ecosystem engineers in carbon burial, where a balance exists between carbon burial and biological processes that release carbon (e.g. calcification) (van der Heijden & Kamenos, 2015). Organic carbon in these systems is

associated with both the calcifying engineer and associated SOC buried in the carbonate deposits that are created by the calcifying organisms. Here we have shown that the quantity of SOC buried in deposits created by calcified vegetated ecosystem engineers is comparable to, if not higher than, other vegetated systems. As would be expected, a degree of SOC breakdown and remineralisation was observed (as a general decline in OC over time). However, this was apparent for only ~500 years, after which the quantity of buried organic carbon stabilised. Importantly, coralline algal ecosystems are found throughout the world's coastal ocean, from the intertidal to 100+ m depth and their deposits are frequently stable for millennia (van der Heijden & Kamenos, 2015), representing a globally significant carbon store relevant at geological timescales. Our results show that this coastal vegetated system has persisted for at least the past 5070 years, and despite abrupt ecosystem shifts during this time, has been actively burying and storing blue carbon for the duration.

Calcifying algae can also be significant components in other vegetated systems. We now know that seagrass meadows, which are recognised blue carbon storage ecosystems (Fourqurean et al., 2012), are also globally significant 'hotspots' of calcium carbonate production because of the abundance of calcifying organisms such as epiphytes (including red coralline algae), benthic invertebrates, carbonate deposition during sedimentation, and direct carbonate formation by some seagrass species (Mazarrasa et al., 2015). Despite this potentially large source of CO_2 release via the calcification process, seagrass meadows likely still exhibit a net drawdown of CO_2 (Macreadie, Serrano, Maher, Duarte, & Beardall, 2017), demonstrating that high carbonate production does not preclude an ecosystem's role in net blue carbon storage. Thus, we suggest that calcifying algal systems may in fact represent a substantial, global-scale blue carbon repository with millennial longevity. We have shown that this carbon burial potential is sensitive to climatic variability (and subsequent biogeochemical effects) at multiple scales, including long-term climate trends, local ecological structure (e.g. terrestrial and marine primary production) and hydrogeology (e.g. sediment dynamics, river discharge).

Conclusions

We suggest that the quantity and variability of carbon burial is dependent upon the stability of ecosystems and their associated organic production. That relationship can be particularly complex because of the varied factors that can influence ecosystem structure, including climatic variability and, more recently, direct human impacts such as land use change and increased nutrient run-off, which can result in an increase in carbon efflux (e.g.

remineralization) (Macreadie et al., 2012). However, at centennial scales (the time scale over which significant amounts of carbon can accumulate) major changes in climate drives ecosystem structure and carbon burial, while land use change appears to increase the variability of carbon burial. The projected 2-4°C warming over the 21st century (IPCC, 2013) would intuitively be expected to lead to an increase in the quantity of carbon buried over coming decades, driven by concurrent increases in metabolic activity and ecosystem production. However, we suggest that such responses will likely be complicated by (1) changes in other environmental parameters (e.g. carbonate chemistry, oxygenation) projected for the end of the century (IPCC, 2013), (2) land use changes which could cause large variability in carbon burial and (3) rapid projected warming which may cause similar ecosystem reorganisation to that seen during the rapid cooling of the LIA, leading to reduced organic carbon supply despite higher productivity.

Data Sharing and Data Accessibility

Data used in this manuscript are available at DOI:10.17632/hgkwvvw43z.1

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